

# Structure determination of the anhydrous form of MIL-3K: a vanadodiphosphonate with a 3D hybrid framework †

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$K(V^VO(H_2O))(V^{IV}O)O\{O_3P-(CH_2)_2-PO_3\}$  (labelled MIL-3K) is a vanado-ethylenediphosphonate whose previously reported hybrid framework reversibly dehydrates. Its anhydrous form ( $KV^{IV}V_2O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K<sub>an</sub>) has been determined from X-ray powder diffraction data in the centrosymmetric triclinic  $P\bar{1}$  (no. 2) space group with lattice parameters:  $a = 7.2375(1)$ ,  $b = 8.1852(1)$ ,  $c = 9.8862(2)$  Å,  $\alpha = 83.2209(9)$ ,  $\beta = 65.223(1)$ ,  $\gamma = 76.492(1)^\circ$ ,  $V = 516.90(2)$ ,  $Z = 2$ .  $R_F^2 = 0.0920$  and  $R_{wp} = 0.0157$ . The two structures of MIL-3K and MIL-3K<sub>an</sub> are quite similar, just the square pyramidal coordination of one vanadium atom of the hydrate transforms into a  $V^VO_4$  tetrahedron in the dehydrated form. This change induces the opening of eight-membered channels delimited by phosphonate tetrahedra and vanadium polyhedra in strict alternation.

## Introduction

During these two last decades, the preparation of solids from an aqueous medium at low temperature or in hydrothermal conditions was very fruitful and both the number and the diversity of new compounds with open-frameworks has dramatically expanded.<sup>1</sup> These recent ones are often hydrated with water molecules encapsulated in the cavities of their structure and/or directly linked to the metal centres. Primarily, the water molecules form hydrogen bonds with the host-framework and the water content depends on the available free volume of the pores. Nevertheless, the chemical nature of their walls also constitutes a very influent factor. For example, the hydrophobic character of the walls of the vanadoterephthalate named MIL-47 prohibits any insertion of water although the free volume is large.<sup>2</sup> Another role of  $H_2O$  is illustrated by a work reported by Morris and co-workers with the water molecules acting as a template of the building units: this is postulated for the D4R units of the organically templated gallophosphate [pyr, O]GaPO-4.<sup>3-4</sup> Lastly, the metallic cations give rise to a great diversity of coordination polyhedra whose the apices are either shared with other polyhedra or terminal. These unconnected apices are generally occupied by water molecules or hydroxyl functions depending on the pH of the medium synthesis. Whatever the protonation state of these terminal oxygen atoms, ionic or neutral moieties are leaving groups easily removable by heating: around 100 °C for the unlinked water molecules, up to 250–300 °C for the hydroxyl functions. The dehydration induces a structural reorganisation whose the magnitude depends of the structural role of the leaving groups in the hydrated compound. It was difficult for a long time to study such phenomena which generally lead to a degradation of the crystals throughout the dehydration. However, correlatively to the improvement of the structure determination methods using powder data, the structural investigation of the anhydrous phases becomes more and more easy.<sup>5-11</sup>

We have recently reported the hydrothermal synthesis and the structure determination of MIL-3K,<sup>12</sup> a vanado-ethylenediphosphonate with hybrid framework formulated  $K(V^VO(H_2O))(V^{IV}O)O\{O_3P-(CH_2)_2-PO_3\}$ . This compound reversibly dehydrates. This paper deals both with the structural investigation of the MIL-3K dehydration process and the comparison between MIL-3K and its anhydrous form  $KV^{IV}V_2O_3\{O_3P-(CH_2)_2-PO_3\}$  labelled MIL-3<sub>an</sub>.

## Experimental

### Synthesis and thermal analysis

MIL-3K was hydrothermally synthesised from a mixture of  $KVO_3$ , ethylenediphosphonic acid and deionized water in the molar ratio 1 : 0.8 : 250 heated one day at 443 K. Further details are given in ref. 12.

TG measurements were performed under oxygen atmosphere using a TA Instruments TGA2050 apparatus (heating rate: 5° min<sup>-1</sup>). The thermogram of MIL-3K (Fig. 1) shows two weight losses: the first one occurring at 120 °C is in good agreement with the dehydration (4.2% measured *versus* 4.58% expected)

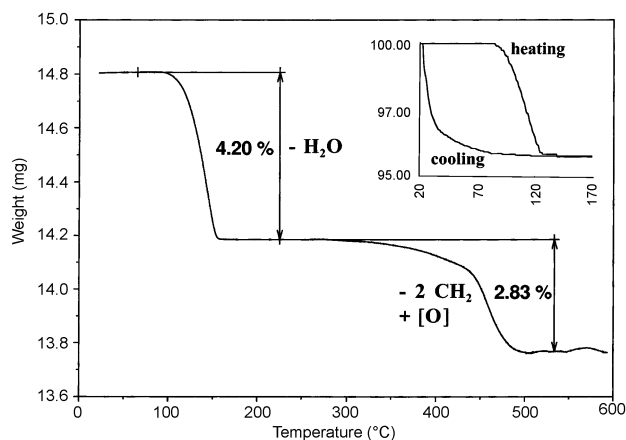


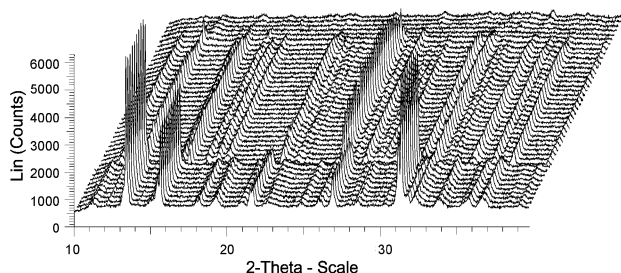
Fig. 1 TG curve of  $K(V^VO(H_2O))(V^{IV}O)O\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K.

† Electronic supplementary information (ESI) available: atomic coordinates and isotropic displacement parameters  $U_{iso}$  (Å<sup>2</sup>) for  $KV^{IV}V_2O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K<sub>an</sub>. See <http://www.rsc.org/suppdata/dt/b2/b205469h/>

whereas the second above 350 °C corresponds to the combustion of the organic part. In a second experiment, the heating was stopped after the first event, then the product was cooled at room temperature. One observes that it recovers its initial weight. So, the dehydration is fully reversible.

### X-Ray powder diffraction

The thermodiffractogram of MIL-3K (Fig. 2) was registered on a Siemens D5000 powder diffractometer using CoK $\alpha$  radiation ( $\lambda = 1.7890$  Å) and equipped with an Anton Parr HTK16 furnace. The heating rate was 1° min<sup>-1</sup> with a step of 10°. The intensities were collected between 10 and 40° (2 $\theta$ ) with a step scan 0.015° (2 s step<sup>-1</sup>). The thermodiffractogram and the TG curve of MIL-3K are in perfect agreement giving the evidence of a structural transformation consecutive to the dehydration. The anhydrous product (MIL-3K<sub>an</sub>) is stable up to the combustion of the ethyl chains then transforms into an amorphous phase.



**Fig. 2** Thermodiffractogram of  $K(V^V O(H_2O))(V^IV O)O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K.

High-resolution powder X-ray diffraction data were collected in transmission mode with a Siemens D5000 diffractometer using Cu-K $\alpha_1$  radiation ( $\lambda = 1.540598$  Å) selected with an incident beam germanium monochromator. The detector was a Braun PSD. The dehydration of MIL-3K is quickly reversible. Therefore, high-resolution powder X-ray diffraction data were collected at 25 °C for a sample encapsulated in a sealed capillary after first being dehydrated at 200 °C for 4 h.

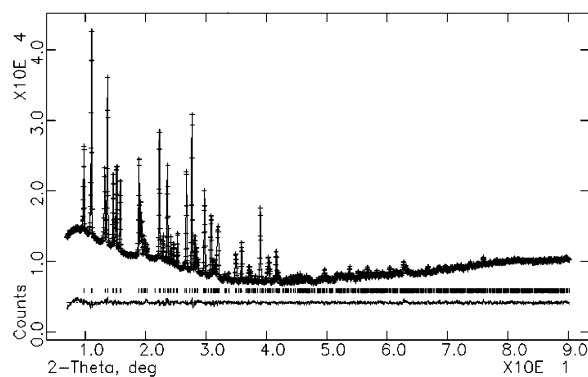
The diffraction pattern was indexed on the basis of the first 20 Bragg reflections with the program TREOR-90,<sup>13</sup> resulting in a triclinic unit cell:  $a = 7.243$ ,  $b = 8.187$ ,  $c = 9.887$  Å,  $\alpha = 83.25$ ,  $\beta = 65.26$  and  $\gamma = 76.5$ ° ( $M_{20} = 48$ ). Assuming space group  $P\bar{1}$  (no. 2), the crystal structure was solved by help of the EXPO program,<sup>14</sup> which integrates the program EXTRA<sup>15</sup> for the extraction of intensities with SIRPOW.92,<sup>16</sup> a direct methods program specially designed for powder data. All the atoms in the unit cell were located from the E-map with the highest figure-of-merit. These atomic positions were thereafter used as starting model for Rietveld refinement using the GSAS program.<sup>17</sup> Initially, scale, background, zero point and lattice parameters were refined. The profile parameters were optimised by first fitting the pattern using the LeBail method. The atomic coordinates were refined by adding soft distance constraints:  $d[V(1)-O(3)] = 1.61(2)$ ,  $d[V(1)-O(1), O(2), O(7), O(8))] = 2.02(4)$ ,  $d[V(2)-O(4), O(6)] = 1.61(2)$ ,  $d[V(2)-O(5), O(9)] = 1.92(3)$ ,  $d(P-O) = 1.53(2)$ ,  $d(P-C) = 1.80(2)$  and  $d(C-C) = 1.52(2)$  Å. In the next stage of the refinement, common isotropic displacement parameters were introduced for P, V, O and C, respectively. This gave satisfactory residual factors of  $R_F^2 = 0.0920$  and  $R_{wp} = 0.0157$  for a total of 89 refined parameters. The weight on the soft constraints could not be removed without unrealistic bond distances emerging in the structure, and was therefore kept at a value of 250 in the last cycles of the refinement. For further details, see Table 1. Atomic coordinates and isotropic displacement parameters are given in Table S1,† selected bond distances in Table 2. Fig. 3 shows the observed, calculated and difference diffraction

**Table 1** Experimental conditions and relevant data for the Rietveld refinements of  $KV^{IVV}O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K<sub>an</sub>

Formula	$KV^{IVV}O_3\{O_3P-(CH_2)_2-PO_3\}$
Formula weight	374.97
Wavelength/Å	1.540598
Space group	$P\bar{1}$ (no. 2)
$a/\text{Å}$	7.2375(1)
$b/\text{Å}$	8.1852(1)
$c/\text{Å}$	9.8862(2)
$\alpha/^\circ$	83.2209(9)
$\beta/^\circ$	65.223(1)
$\gamma/^\circ$	76.492(1)
$V/\text{Å}^3$	516.90(2)
Z	2
Observations	5390
Reflections	872
Refined parameters	89
$R_{wp}$	0.0157
$R_F^2$	0.0920

**Table 2** Principal interatomic distances (Å) in  $KV^{IVV}O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K<sub>an</sub>

Vanadium polyhedra	Diphosphonate units	K <sup>+</sup> neighbouring
V(1)-O(3): 1.606(6)	P(1)-O(7): 1.495(6)	K-O(3): 2.752(7)
V(1)-O(1): 1.965(8)	P(1)-O(8): 1.509(6)	K-O(4): 2.787(9)
V(1)-O(7): 1.979(7)	P(1)-O(9): 1.517(6)	K-O(4): 2.840(9)
V(1)-O(2): 2.010(8)	P(1)-C(2): 1.797(7)	K-O(2): 2.94(1)
V(1)-O(8): 2.016(9)	C(2)-C(2): 1.500(8)	K-O(6): 3.020(7)
V(1)-O(4): 2.45(1)		K-O(8): 3.038(9)
	P(2)-O(2): 1.513(6)	K-O(6): 3.04(1)
V(2)-O(4): 1.596(6)	P(2)-O(1): 1.516(6)	K-O(7): 3.15(1)
V(2)-O(6): 1.623(6)	P(2)-O(5): 1.526(6)	
V(2)-O(5): 1.888(7)	P(2)-C(1): 1.803(7)	
V(2)-O(9): 1.928(7)	C(1)-C(1): 1.497(8)	



**Fig. 3** Final Rietveld plot of  $KV^{IVV}O_3\{O_3P-(CH_2)_2-PO_3\}$  or MIL-3K<sub>an</sub>.

profiles from the Rietveld analysis of data for  $KV^{IVV}O_3\{O_3P-(CH_2)_2-PO_3\}$ .

CCDC reference number 180510.

See <http://www.rsc.org/suppdata/dt/b2/b205469h/> for crystallographic data in CIF or other electronic format.

### Discussion

MIL-3K<sub>an</sub> presents a pillared structure built up from the stacking along [010] of inorganic layers connected *via* the organic ethyl chains (Fig. 4). Inside the layers, the vanadium atoms are localised on two different crystallographic sites: V(1) and V(2) are six and four-fold coordinated respectively in a VO<sub>6</sub> octahedron and in a VO<sub>4</sub> tetrahedron (Table 2). Valence bond calculations<sup>18</sup> unambiguously show that V(1) and V(2) are at the oxidation states +4 and +5 respectively. Each VO<sub>6</sub> octahedron shares four oxygen atoms of its basal plane with four PO<sub>3</sub>C tetrahedra of four different diphosphonate groups to form mixed chains running along [001] (Fig. 5) and the fifth one with

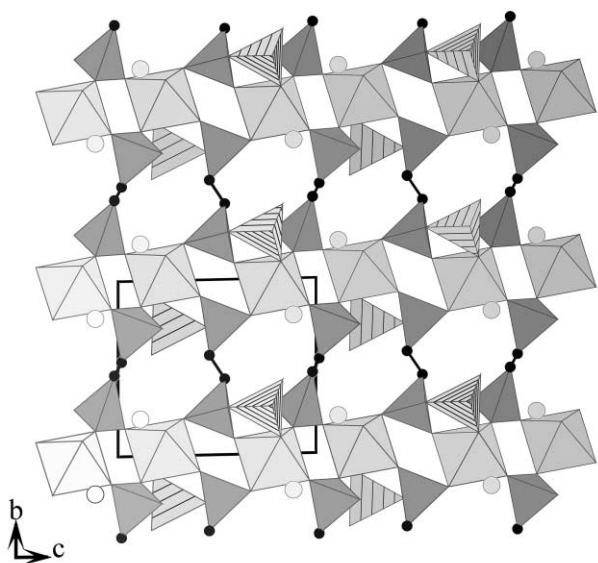


Fig. 4 Projection of the structure of MIL-3K<sub>an</sub> along [100] showing its pillared feature (hatched polyhedra for the vanadium atoms whose the coordination changes throughout the dehydration).

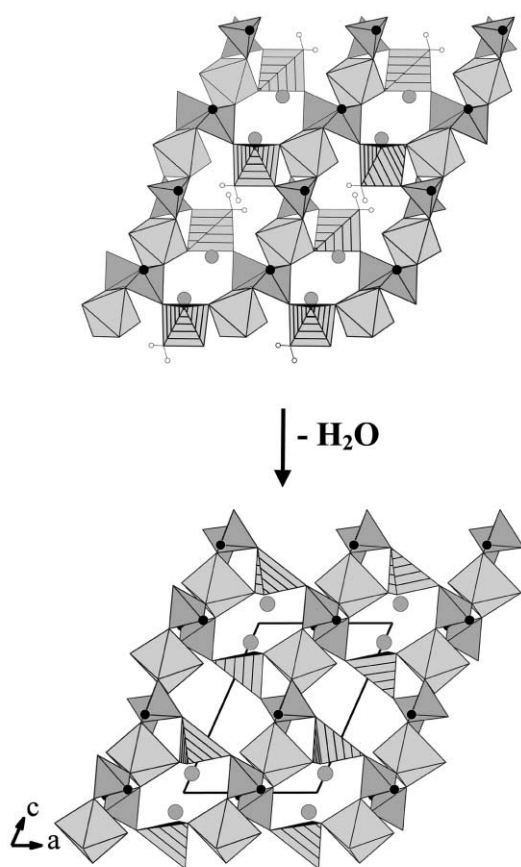


Fig. 5 Projection of one inorganic layer of MIL-3K<sub>an</sub> (bottom), identical view for the hydrated phase MIL-3K (top) (hatched polyhedra are VO<sub>4</sub>(H<sub>2</sub>O) square pyramids then VO<sub>4</sub> tetrahedra in MIL-3K then MIL-3K<sub>an</sub> respectively).

a V(2)O<sub>4</sub> square pyramid; the remaining apex is terminal. This last one corresponds to a short vanadyl linkage (V–O = 1.606(6) Å). The phosphorus atoms are tetrahedrally coordinated with three P–O distances in the range 1.495(6)–1.526(6) Å and a longer P–C distance around 1.8 Å as usually encountered in the alkylphosphonate units. The carbon atoms point on the both sides of the mixed chains and so ensure the three-dimensionality of the framework. The connection of the mixed

chains by the VO<sub>4</sub> tetrahedra generates perforated inorganic slabs exhibiting two types of windows. The six-membered windows delimited by two octahedra, two square pyramids and two tetrahedra are filled by the K<sup>+</sup> cation performing a similar eight-fold coordination as in the hydrated MIL-3K compound. On the other hand, the second type of windows is consecutive to the departure of the water molecules and does not exist in the hydrated phase. Indeed, in MIL-3K (Fig. 5), V(2) is five-fold coordinated with a water molecule in terminal position whose the elimination transforms the coordination of V(2) from square pyramidal in MIL-3K to tetrahedral in MIL-3K<sub>an</sub> and allows the formation of these new windows free of occluded moieties. It is worth noting that this transformation does not change the oxidation state of the vanadium which remains +5.

The same type of transformation just involving an evolution of the coordination polyhedra was already reported with the dehydration of the organically templated ferric phosphate ULM-12 into ULM-19.<sup>6</sup> The framework of ULM-12 is described by the corner-connection of (i) hexamers containing one ferric trimer of octahedra, and (ii) dimers containing one FeO<sub>4</sub>(H<sub>2</sub>O) square pyramid and one phosphate group. The dehydration deals with the elimination of the terminal water molecules in such a way that of the two external octahedra one becomes a square pyramid and the other a trigonal bipyramid; the square pyramid becomes a Fe<sup>III</sup>O<sub>4</sub> tetrahedron. Sometimes, the dehydration leads to an unstable edifice whose the relaxation involves a structural rearrangement. In the 3D zincomethylendiphosphonate MIL-48,<sup>8</sup> the departure of the water molecules located in the channels requires a partial rearrangement of the structure: the two ZnO<sub>4</sub> tetrahedra of the hexameric building units collapse into a Zn<sub>2</sub>O<sub>8</sub> dimer of two edge-shared square pyramids. The nickeldiphosphonate VSB-2<sup>7</sup> presents a particular feature since the elimination of all the water molecules linked to the different Ni<sup>2+</sup> cations occurs in two steps. In a first stage, the partial dehydration implies a large structural rearrangement since it transforms the lamellar compound VSB-2 into a three-dimensional framework labelled VSB-3. The second step leads to the anhydrous VSB-4 compound just differing from VSB-3 by the coordination polyhedra of one nickel atom (square pyramidal instead of octahedral).

## Conclusion

This paper deals with the structure determination of the anhydrous form of the vanadodiphosphonate MIL-3K. It is shown that the dehydration generates few structural modifications but allows the opening of new channels in the hybrid framework. Such a study was already described concerning the combustion of the templates in the organically templated microporous compounds. This is of particular interest when the elimination of the template does not lead to an amorphous phase but to a compound with effective microporous properties. A very nice example was recently provided by the gallophosphate MIL-34<sup>19</sup> whose the three-dimensional framework inserts cyclobutylammonium cations. The structure of the calcined sample was first predicted from lattice energy minimization then used as starting model for the Rietveld refinement. This study is very innovative and opens the way to methods combining the numerical simulation with the diffraction technics. Such an approach is also suitable for the structural investigations of the dehydration processes.

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